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Cluster size and Excitation wavelength dependent Photoluminescence behavior of nano colloidal Ge- Se- Sb- Ga chalcogenide glass solutions

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The photoluminescence emission characteristics from Ge- Se- Sb- Ga nano colloid chalcogenide glass solutions were investigated and the results obtained are presented. The spectra show a remarkable dependence on the chalcogenide glass concentration (0.72mg to 0.12 mg in 1ml amine solvent) and the excitation wavelength (350 nm-560 nm). The energy gap of the nano colloid solutions were found to depend on cluster size which in turn depend on concentration of chalcogenide glass in solution. We have found there is a cluster size and excitation wavelength dependent shift of the luminescence peak. The excitation at the tail of the absorption band gives rise to an emission that shifts with the change of the excitation wavelength. The significant feature of this photoluminescence from these samples can be attributed to the electronic states in the bandgap of the nano colloidal solutions.

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1. Introduction

Chalcogenide glasses have emerged as promising candidates for multifunctional devices due to their low phonon energy, high transparency in infrared, large nonlinear refractive indices, ability to produce fibers etc [1-**3**]. Most of the optical studies on chalcogenide glasses were done on thin films prepared by vacuum coating techniques (thermal evaporation or sputtering) or pulsed laser deposition from bulk glass [4-6]. The possibility of tailoring bulk material properties by varying the size, structure and composition of the constituent nanoscale particles make them an interesting candidate for various important applications in the field of new material research [7]. Understanding the size-dependent optical properties of semiconductor chalcogenide glass clusters had been achieved and found to be applicable in different optical applications [8,9]. Photoluminescence (PL) study on chalcogenide glasses is an obvious technique for investigating information regarding the nature of localized electronic states within the band gap. Such a study will contribute greatly towards a complete description of the electrical and optical properties of the glassy systems [10]. Recent studies show that nano-structured thin films with luminescence properties are promising materials in many applications such as flat panel displays, light-emitting devices, optoelectronic and photonic devices etc [11].The incorporation of inorganic quantum dots (QDs) into organic light-emitting devices (OLED) as efficient lumophores has recently attracted considerable attention. Since the first experimental demonstration in the mid 1990s on quantum cascade (QC) lasers, they have continued to grow due to their versatility and high performance. QC lasers have become a central component in the development of mid-infrared sensing applications [12]. High power and room temperature operation make QC lasers a promising choice for trace-gas detection in the mid-infrared where the spectroscopic “fingerprints” of most atmospheric trace gas are found.

Shanshan Song et al [12] have reported a QC laser using nano colloid As-S which can be tuned without changing the temperature. The luminescence property of the nano colloid chalcogenide glass used for cascading is an important property which has to be considered in detail. The quantum size effect on the luminescence property of Ag–As–Se nano-sized clusters was recently reported by Congji Zha et al [13].The intention of the present work is to study the dependence of the photoluminescence (PL) on the energy of the exciting radiation.

2. Experimental studies

The chalcogenide glass of composition $Ga_5Sb_{10}Ge_{25}Se_{60}$ was prepared by melt quenching method from elements of 5 N purity weighed in pre-cleaned fused quartz ampoule in the required molar ratio. The evacuated and sealed ampoule was placed in a rocking furnace and heated at temperature of 1150°C for 24h. The $Ga_5Sb_{10}Ge_{25}Se_{60}$ melt was then ice water cooled to obtain the chalcogenide bulk glass. The amorphous nature and the composition of the prepared bulk glass were found Using X-ray diffraction (XRD) technique (Bruker AXS D8 Advance X-ray Diffractometer) and energy-dispersive X-ray spectroscopy (EDS) respectively. From the composition analysis it was found that the composition of the prepared glass was identical to the initial concentrations introduced in the batch. The nano-colloidal glass solutions were prepared with five different concentrations and named as C_0, $C_{1,}$ $C_{2,}$ $C_{3,}$ C_4 (C_0=0.72mg/ml, C_1=0.67 mg/ ml, C_2=0.540 mg/ml, C_3=0.335 mg/ml and C_4=0.12 mg/ml.). The nano colloidal solutions of $Ga_5Sb_{10}Ge_{25}Se_{60}$ were obtained by dissolution of bulk glass in n- butylamine solvent (Sigma-Aldrich, 99.9%).The dissolution was carried out inside a sealed glass container to prevent solvent evaporation. The dissolution and clustering mechanisms are described elsewhere [14]. The NMR (Bruker Avance III, 400MHz) spectra were taken to confirm the formation of chalcogenide glass clusters at the time of dissolution.

The solutions were characterized by optical absorption measurements recorded by using a spectrophotometer (JascoV-570 UV/VIS/IR) and the fluorescence emission measurements were recorded by using a Cary Eclipse fluorescence spectrophotometer (VARIAN). The photoluminescence behaviour of nano colloidal chalcogenide glasses have been studied as a function of excitation wavelength and cluster size. Scanning Electron Microscope (SEM) (JEOL Model JSM - 6390LV) photographs of two selected solutions were taken to understand the distribution of the nanoclusters. The emission from the clusters were confirmed from the confocal microscopy (Leica TCS SP5 LASER scanning confocal microscope) of the solutions.

Laser induced Pl studies were carried out in the nano colloid solutions using a frequency doubled Nd:YAG laser. The samples were transversely pumped using 7 ns pulses from a frequency doubled Nd:YAG laser (532 nm, 10 Hz). The emission from the sample was collected by a fibre and directed to a 0.5 m spectrograph (SpectraPro-500i) coupled with a cooled CCD array. The experimental set up is explained elsewhere [15].

3. Results and discussion

The absorption spectra of chalcogenide glass solutions are presented in Fig. 1. Optical bandgap (E_g) was found from the exponential fit of absorption data in the Urbach tail region. The optical bandgap of the solutions were also estimated using the derivatives of the transmission curves. The shift in the absorption edge is due to the change in cluster size with concentration. From the SEM analysis it was found that with increasing concentration of $Ga_5Sb_{10}Ge_{25}Se_{60}$ glass the cluster size also increases. The dependence of the bandgap with cluster size of nanocolloid solution was reported earlier [14] .The nanocluster formation in the solution is shown in Figure 2(a). The cluster size from the SEM analysis on spin coated thin films of the solution was found to be around 70 nm and 40 nm for C_1 and C_3, respectively [14]. The ^1H NMR spectra was taken to check whether amine salts are present in the colloid solutions and is presented in figure 2(b). The chemical shift (around 7.5) as shown in Figure 2(b) shows the prescence of salt formation in the solution.

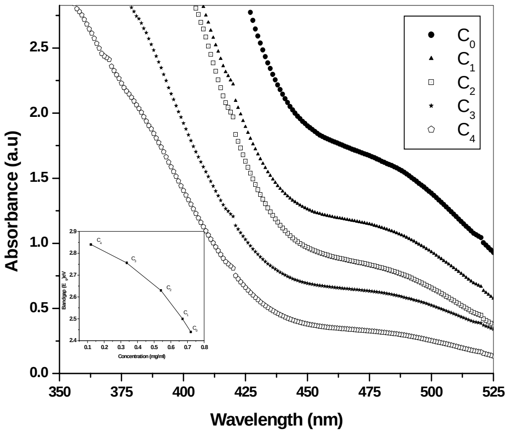
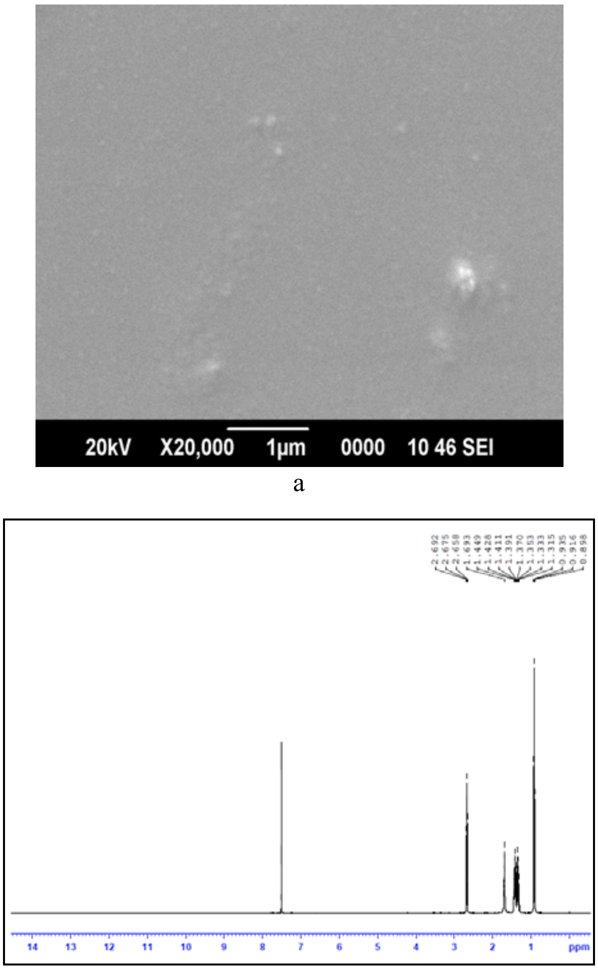


Fig. 1. Absorption spectra of nano colloids $Ga_5Sb_{10}Ge_{25}Se_{60}$ chalcogenide glass. Inset shows the dependence of the bandgap with the concentration.

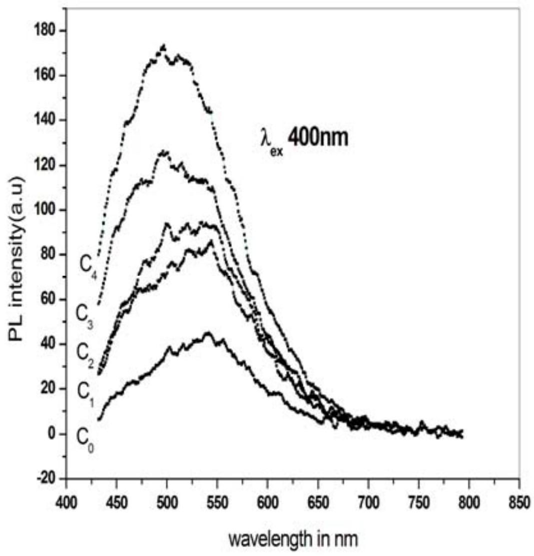


a

b

Fig. 2. (a)SEM image showing the nano ranged cluster formation in the chalcogenide glass solution (C_1 = 0.67 mg/ml). The cluster size for C_1 is around 70nm.(b) NMR spectrum of C_1.

The slope of the absorption edge characterizes the width of the localized states which in turn indicates the ordering of the structure. It is believed that the charged defects and localized states exist in the bandgap of amorphous systems [10]. Due to these bandgap states in chalcogenide glasses the optical transitions such as photoluminescence (PL) and the optical absorption process are complicated in glassy systems. Figure 3(a) presents the photoluminescence spectra of nano colloidal solutions of $Ga_5Sb_{10}Ge_{25}Se_{60}$ at an excitation of 400nm.



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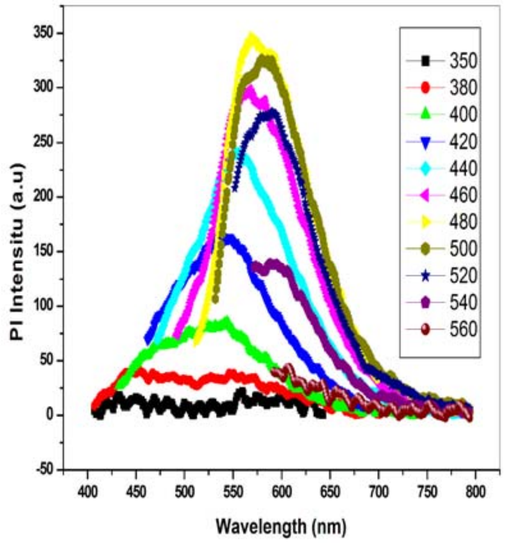

b

Fig. 3. (a) PLspectra of nano colloid $Ga_5Sb_{10}Ge_{25}Se_{60}$ at an excitation of 400nm. (b) excitation wavelength dependent PL shift for nano colloid $Ga_5Sb_{10}Ge_{25}Se_{60}$ at a concentration of 0.67mg/ml (C_1) .

The photoluminescence spectra shows a cluster size dependent change in peak wavelength and intensity .It is found that for excitation at 400nm the photoluminescence intensity increases with decrease in cluster size(due to decrease in concentration). Lesser the concentration smaller will be the broadening of the band tails. The excitation wavelength dependent change in photoluminescence in C_1 is given in figure 3(b). Figure shows a remarkable dependence on the cluster size of the nano colloid glass solution investigated and the excitation energy. A strong electron phonon coupling distorts the lattice near the trapped hole and this interaction is responsible for the broadness of the luminescence band [16-18].

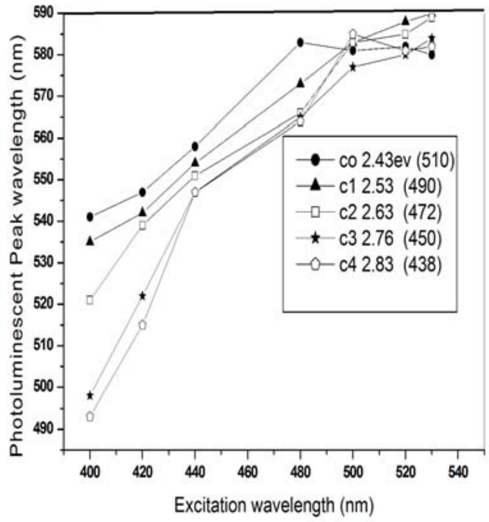

Fig. 4. PL peak wavelength versus excitation wavelength plots of nano colloids $Ga_5Sb_{10}Ge_{25}Se_{60}$ chalcogenide glass solution.

Studies by Street et al [10] shows that the broad luminescence spectra is common in chalcogenide glasses and they proposed the model of negative-U defects, which can explain many PL-related properties in chalcogenide glasses. They considered that the charged defects (D+ and D−) are formed in the chalcogenide glasses due to strong coupling between electrons and the lattice. These charged defects, which have energy levels in the bandgap with a spectral bandwidth ΔE, are responsible for the PL in chalcogenide glasses. The excitation energy dependence of Photoluminescence intensity in Ge -S glass was reported by M Seki et al [19].It can be noted that [figure 3 (b)], as the excitation wavelength (λ_{ex}) increases the PL peak intensity increases upon to an optimum wavelength ,thereafter the intensity again decreases. The PL dependence on λ_{ex} provides the spectral response of the luminescence centers formed by the defects as explained above .When the excitation is with optimum λ_{ex} only then the electronic transitionprobability from the charged centres to the conduction band is maximum which leads to maximum PL intensity[20-22]. In other words spectra 3(b) help us to gain information regarding the spectral response of the photoluminescence centre. In fact the significance of this band is seen in absorption spectra (figure 1) in the region 400nm -540nm. Another important result to be noted is that before the optimum excitation concentrated $Ga_5Sb_{10}Ge_{25}Se_{60}$ nano colloid solution ie, C_0 is having higher PL intensity whereas after the optimum excitation the PL intensity increases with the decrease in concentration. Figure 5a shows the PL spectrum for nano colloid solutions obtained at an excitation of 532 nm. In order to check this result the PL intensity with three different concentration were also studied using a Nd: YAG laser beam and the PL spectra obtained for these concentrations is presented in figure 5(b). It is found that at 532nm the higher concentration is having more photoluminescence intensity compared to lower concentration. Here as the concentration increases the non radiative relaxation of the excited state to the defect centres is seen to overcome radiative relaxation above an optimum concentration. The non radiative relaxation originating by the collision process enhances with the concentration therefore when we monitor the PL intensity as the function of concentration PL quenching takes place. In bulk samples the decrease in such quantum efficiency at higher excitation energy has been explained due to strong non radiative surface recombination [23].

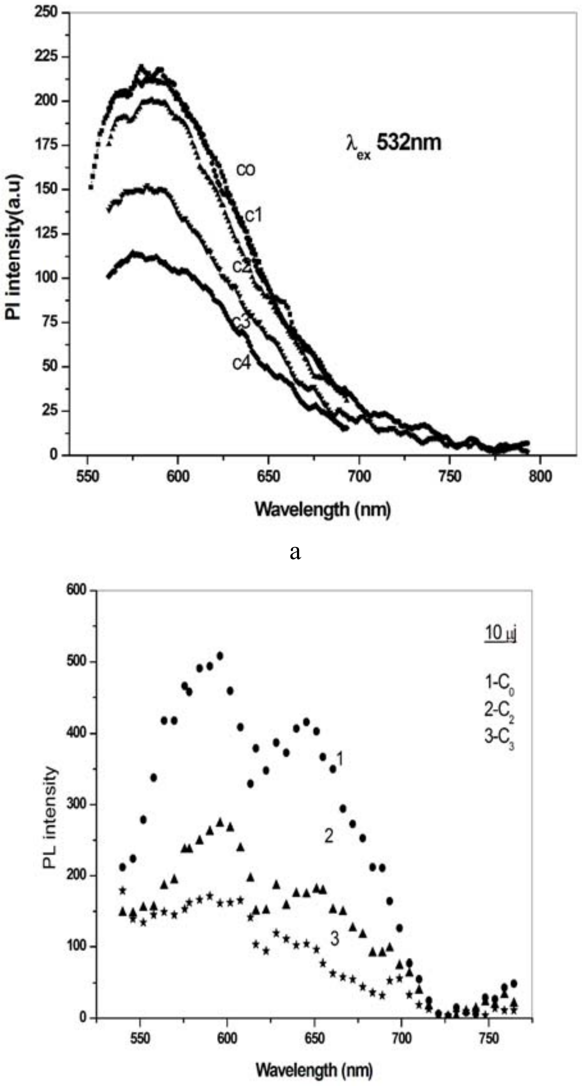

Fig. 5. (a) PL spectra of nano colloid $Ga_5Sb_{10}Ge_{25}Se_{60}$ at an excitation of 532nm (b) Emission from the samples at pump energy of 10μJ from an Nd:YAG laser.

In order to confirm the emission from the clusters of nanocolloid chalcogenide glass solution confocal microscope imaging was done. A representation of the emission from the C_o concentration is given in Fig. 6.

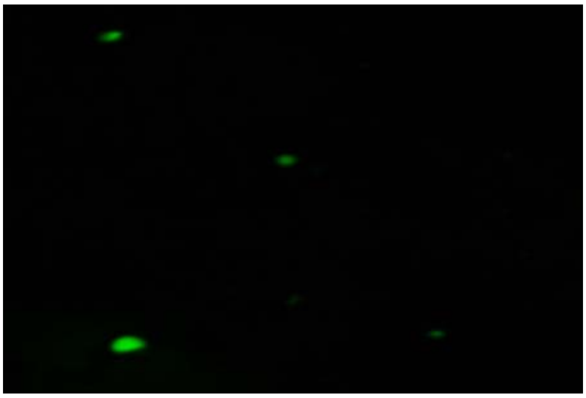

Fig. 6. Confocal microscope image showing the emission from the nano colloid chalcogenide glass clusters at an excitation with 484nm.

4. Conclusions

In conclusion, we have presented excitation wavelength-dependent and concentration dependent photoluminescence shift in chalcogenide nano colloid solution based on $Ga_5Sb_{10}Ge_{25}Se_{60}$ glass. The bandgap dependence based on the cluster size of the nano colloid $Ga_5Sb_{10}Ge_{25}Se_{60}$ solutions are explained using absorption spectroscopy. The PL studies show that the localized states differ with the concentration and those defect states play an important role in the luminescence spectra. There exists an optimum excitation wavelength at which the emission intensity is maximum. The quenching of the luminescence intensity after a particular excitation has been explained due to the presence of the non radiative recombination. Studies show that these materials are promising candidates for light-emitting devices and optoelectronic devices.

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